






**METHOD FOR TRANSESTERIFICATION OF FATS AND/OR OILS BY MEANS OF ALCOHOLYSIS**





**Patent number:** WO03004591 (A1)  
**Publication date:** 2003-01-16  
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**Classification:**  
- **international:** **C07C67/03; C11C3/04; C11C3/10; C07C67/00; C11C3/00;**  
(IPC1-7): C11C3/04; C11C3/10  
- **european:** C07C67/03; C11C3/04; C11C3/10  
**Application number:** WO2002EP07311 20020702  
**Priority number(s):** DE20011032842 20010706

**Also published as:**

 DE10132842 (C1)  
 EP1358306 (A1)  
 EP1358306 (B1)  
 CN1496398 (A)  
 US2004059143 (A1)

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**Cited documents:**

 CA2131654 (A1)  
 WO0112581 (A1)  
 GB575416 (A)  
 XP002163432 (A)

**Abstract of WO 03004591 (A1)**

The invention relates to a method for obtaining fatty acid esters, from triacyl glycerides by means of alcoholysis. The invention particularly relates to a method of the transesterification of fats and/or oils by alcoholysis, in which at least one alkyl fatty acid ester is added in such an amount during the initial phase that the resulting reaction mixture is a single phase. A higher reaction rate can thus be achieved with the method thereafter.

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Method to the transesterification of fat and/or oil by means of alcoholysis the invention relates to a method to the recovery of fatty acid esters from Triacylglyceriden by means of alcoholysis. In particular the invention concerns a method to the transesterification of fat and/or oil by alcoholysis, becomes added with which the acceleration of the method in the initial phase at least a Alkanolfettsäureester in such an amount that the reaction mixture resultant thereby becomes single-phase.

Transesterification reactions actual are known. They represent a commercial significant class industrial organic reactions. With a transesterification reaction an ester becomes by exchange of the acid groups or transferred by exchange of the alkoholschen groups into another ester. If the transesterification becomes made by exchange of the alcoholic groups, one speaks of the so called alcoholysis (also Alkanolyse). With the alcoholysis the alcohol becomes and/or. the alkanols in the excess added, around an high yield at the desired ester to be obtained. In newer time the preparation of alkyl star, in particular from methyl esters, has by vegetabilische oils in connection with the generation of diesel fuel from regenerating raw materials (z. B. Rapeseed oil, soya oil), significant at topicality recovered.

The transesterification is an equilibrium reaction, which becomes usually already the triggered by mixing reactants. The reaction runs however so slow that is usually required for the commercial execution of the reaction a catalyst. As catalysts serve usually strong acidic ones or strong bases.

Fats and oils consist predominant of Glyceriden (mono, Di-und triglycerides).

With the transesterification of such fats and oils the component can become glycerol by low molecular monohydric alcohols substituted. In the practice for this the frequent method becomes applied after Bradshaw (described in the US patents 2, 271, 619 and 2, 360, 844). The reaction becomes conducted in an open container, which can consist of ordinary carbon steel. The fat or oil must be drying (anhydrous), clean and above all neutral, D. h. that content at free fatty acids must be more negligible small (acid value not higher as 1, 5). Generally the monohydric alcohol in high excess becomes added the increase of the yield and the reaction rate the reaction mixture (the equivalent ratio is often higher as 1: 6).

In a work of WRIGHT et al. (HJ. WRIGHT, J. B. Segur, H. V. Clark, S. K. Coburn, E. E. Langdon and R. N. DuPuis, oil & Soap, 21 [1944] 145-148) became the exact conditions for the alcoholysis of fats with methanol and ethanol in the detail investigated. Further reported becomes from the authors over experiments over the alcoholysis with other monohydric alcohols. It becomes stated that the described above alcoholysis catalyzed with alkali is complete successful only if the fat is almost free of free fatty acids and the reaction mixture free of water. If one of these conditions is not met, it comes to the saponification, which has a loss to alkalinity and the formation of a gel structure to the sequence, those the separation and the settling of the glycerol prevented or slowed.

The transesterification of the Triacylglyceride by means of alcoholysis is characterised in that the reaction between alkanols and Triacylglyceriden of a start-up phase requires, in which only a small reaction rate exists, because the reaction component is not alkanols in the oil soluble. Particularly with the preparation of methyl esters this circumstance is very disturbing, since methanol is only little soluble in the umzuesternden oils and fats. On the other hand methanol is in the methyl esters of the fatty acids good soluble. Pathways of the small methanol concentration in the oil the transesterification reaction runs off only slow one. The reaction mixture must become vigorous mixed to finally that content at esters so far rose that the reaction mixture becomes single-phase and the reaction rate sudden strong rises.

▲ top

As catalysts alkali metals or alcoholates of the alkali metals become used in the practice. The alkaline catalysts dissolve in the reaction mixture, D. h. the reaction becomes homogeneous catalyzed. The alkali metals and their alcoholates become in courses of the reaction soaps the reacted, which particularly separate in the resultant glycerol and whose subsequent treatment to pure glycerol raise the price of. In addition, in the methyl ester remain small amounts at alkali, which might not be problem-free whole with the use of the methyl esters as diesel fuel. Therefore also heterogeneous catalyzed methods became, z in newer time. B. using a metal salt of a strong basic amino acid as solid catalyst proposed (patent application DE 199 50 593 aluminium), insoluble in the reaction mixture.

Furthermore a catalyst on basis of titanium oxides became developed, which it has the disadvantage that the reaction temperatures lie within the range of 240 C.

On the basis of this state of the art it is to be eliminated the object of the invention this start-up phase with moderate reaction temperatures and/or. to shorten and to arrange the method thereby more effective.

The solution of this object made by a method to the transesterification of fat and/or oil by means of alcoholysis, with which the umzuesternden fat and/or oil the execution of the alcoholysis alkanols become, in particular univalent

alkanols in the excess added, characterised in that the fat and/or the oil at least a Alkanolfettsäureester in such an amount added become that the reaction mixture resultant thereby becomes single-phase with reaction conditions.

Surprisingly it was now found that already a right small amount at supplied Alkanolfettsäureestern knows a this solve the problem. The addition of the Alkanolfettsäureester can take place at it forwards, after or simultaneous with the addition of the alkanols.

After the method of this invention the initial phase becomes avoided with the transesterification thereby and/or. shortened that for example becomes added for the case of the alcoholysis with methanol a part of the continuous generated methyl esters the starting product at Triacylglyceriden in such amounts that the mixture becomes single-phase from oil, methanol and methyl ester.

If the reaction mixture in a single phase is present, the effective Alkanolkonzentration is high from the outset and the reaction runs off corresponding fast. For example a reaction rate of 0,8 g/skgznarg and after entry of single-phasesness became a reaction rate of 2,5 g/skgznarg measured with 135 C in the initial phase of a catalyzed process heterogeneous with Zinkarginat (methyl ester production from palm oil).

The fat and/or oil, which in the invention process used becomes, can be in particular biological origin.

The amount at Alkanolfettsäureestern, which must become the preparation of a single-phase mixture added, depends on the quality of the oil, the height of the Alkanolüberschusses and the reaction temperature. The Alkanolüberschuss becomes the increase of the reaction rate and the yield at fatty acid alkane oil star generally with an equivalent ratio (D. h. Ratio of mol fatty acids in the fat and/or oil to mol univalent alkanols) of 1: 6 or over it applied.

Alkanolfettsäureester, which in the method preferably added becomes, are z. B. Methyl ester, ethyl ester and/or Propylester.

The Alkanolfettsäureester preferably becomes in an amount from 5 to 50 Gew. - %, particularly preferred 12 to 20 thread. - % related to the fat and/or oil zugege users.

The invention process is particularly effective, if intended is, the transesterification in an heterogeneous catalyzed process, which preferably continuous can be to operate. In addition, with an homogeneous catalyzed method the method is favourable after this invention, because the costs for the swirl of the two phases in the initial phase of the reaction saved to become to be able. Such heterogeneous catalyzed methods become for example in the mentioned above DE 199 50 593 described.

Thus a catalyst becomes added in an other preferable embodiment the method, which can be either a soluble catalyst or in alkanols and in the reaction mixture insoluble metal salt of a amino acid or an amino acid derivative.

The solved catalyst can exist for example in solved alkali metals or Alkoholten of alkali metals.

The insoluble catalyst can exhibit a metal component, which is calcium, strontium, barium, another alkaline earth metal, or heavy metal, in particular silver, copper, zinc, manganese, iron, nickel, cobalt, lanthanum or another rare earth metal, while the amino acid component of the insoluble catalyst can contain quarternären nitrogen or a Guanidinogruppe. Particularly preferred is the insoluble catalyst a Schwermetallsalz of the arginine, in particular the zinc salt or the cadmium salt of the arginine. , The catalytic active salts insoluble in the reaction mixture can be depressed thereby on a suitable carrier.

The invention process can be accomplished to particularly effective, if the portion of free fatty acids in that umzuesterndem fat and/or oil less than 0.5 Gew. - %, in particular less than 0.1 Gew. - amounts to %.

In addition it was found that the reaction temperatures should preferably lie with the heterogeneous catalyzed transesterification within the range of 80 to 160 C, in particular within the range of 100 to 150 C.

Particularly preferred becomes in the invention process a procedure, becomes recirculated with which the Alkanolfettsäureester, which stays after separation of the glycerol from the product stream with the subsequent separation and purification of the major amount of the generated methyl esters by distillation as Sumpffprodukt. In this way simultaneous small amounts at not reacted Glyceriden become recirculated. In addition becomes corresponding elevated thereby the Glyciergehalt in the final phase of the reaction reduced and the yield of the equilibrium reaction. Altogether so a continuous processing becomes possible.

The amount at methyl esters, which is to the preparation of single-phasesness with reaction temperatures within the range of 100 to 150 C preferred, amounts to approx. 12 to 20 Gew. - %.

Subsequent one becomes the invention process at different examples near explained.

Thus the invention process at a mixture became from sunflower oil and methanol tested. In this case was sufficient for fatty acids in the oil with 135 C and an equivalent ratio of mol to methanol of 1: 6 (60 Gew. - % sunflower oil and 40 Gew. - % methanol) an addition of approx. 15% Gew. - % methyl ester related to the oil, in order to produce an a phase system. The adjusting pressure amounted to in the described case 5 bar. As catalyst Zinkarginat served. The reaction rate amounted to 2,5 g/skgznarg. In this example from the beginning an high reaction rate became obtained.

In addition palm oil became with 150 C with methanol in the equivalent ratio of 1: 6 mixed and Zinkarginat as catalyst added. After addition of 20 Gew. - % Methyl ester concerning palm oil was single-phase the mixture. The reaction rate was with 3,2 g/skgznarg from the beginning high. The initial phase with low reaction rate was jumped over.

Palm oil became further with 85 C with methanol in the equivalent ratio of 1: 6 mixed and Zinkarginat as catalyst added. The reaction rate amounted to 0.05 g/skgznarg. After by addition of methyl ester (approx. 13 Gew. - % concerning oil) the reaction mixture was single-phase, became with ambient pressure a reaction rate of 0,35

g/skgznarg measured.

With reaction temperatures from 200 to 240 C 198 03 053 CI become methods with zinc soaps, described, as catalysts with printing up to 90 bar of triglycerides with high equivalent excess at methanol after in the German patent specification DE (equivalent ratio higher as 1: 6) to esters reacted. Bottom these conditions is a higher methyl ester content emergency little, in order to manufacture an a phase system, than in the example mentioned with 135 C.



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- Claims 1. Method to the transesterification of fat and/or oil by means of alcoholysis, with which the umzuesternden fat and/or oil execution the aluminium becomes koholyse alkanols, in particular univalent alkanols in the excess added, characterised in that the fat and/or oil min destens a Alkanolfettsäureester in such an amount added becomes that the reaction mixture resultant thereby becomes single-phase.
2. Process according to claim 1, characterised in that the admitted Alkanolfettsäureester selected becomes from the group, existing from ME thylestern, ethyl esters and/or Propylestern.
3. Process according to claim 1 or 2, characterised in that of the aluminium more kanolfettsäureester in an amount from 5 to 50 Gew. - %, preferably 12 to 20 Gew. - becomes % related to the fat and/or oil added.
4. Process according to one of claims 1 to 3, characterised in that for the execution of the reaction in the reaction mixture of soluble Ka talysator added becomes.
5. Process according to one of claims 1 to 3, characterised in that for the execution of the reaction the reaction mixture in Alkano len and in the reaction mixture insoluble metal salt of a amino acid or an amino acid derivative an added becomes.
6. Process according to claim 4, characterised in that the alcoholysis by solved alkali metals or alcoholates of the alkali metals catalyzed becomes.
7. Process according to claim 5, characterised in that the Metallkom ponente the catalyst calcium, strontium, barium, another earth alkene limetall or an heavy metal, in particular silver, copper, zinc, manganese, Iron, nickel, cobalt, lanthanum or another rare earth metal are.
8. Process according to one of claims 5 or 7, characterised in that the amino acid component of the catalyst quarternären nitrogen or a Guanidinogruppe contains.
9. Process according to one of claims 5 or 7, characterised in that the catalyst a Schwermetallsalz of the arginine, in particular that Zinc salt or the cadmium salt of the arginine is.
10. Process according to one of claims 1 to 9, characterised in that the portion of free fatty acids in that umzuesterndem fat and/or oil less than 0.5 thread. - %, in particular less than 0.1 thread. - amounts to %.
11. Process according to one of claims 1 to 10, characterised in that the transesterification with temperatures in the range from 80 to 160 C, preferably in the range from 100 to 150 C conducted becomes.
12. Process according to one of claims 1 to 11, characterised in that that is liert the reaction mixture added Alkanolfettsäureester from the product stream into the method, resultant with the transesterification, rezirku.

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